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LUBRICITY OF JET FUELS

ESSO RESEARCH AND ENGINEERING COMPANY
PRODUCTS RESEARCH DIVISION • LINDEN, NEW JERSEY

QUARTERLY REPORT NO. 3 – 15 NOVEMBER, 1965 – 15 FEBRUARY, 1966

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WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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LUBRICITY PROPERTIES

OF

HIGH-TEMPERATURE

JET FUELS

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QUARTERLY PROGRESS REPORT No. 3
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FOR

Air Force Aero Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Wright Patterson Air Force Base, Ohio

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FOREWORD

This report was prepared by the Advanced Lubrication Project, Products Research Division, Esso Research and Engineering Co. at Linden, N. J. under Contract AF33 (615) 2828. This program is administered by the Air Force Aero Propulsion Laboratory, Research and Technology Division, Air Force Systems Command with Arthur F. Levenstein, 1/LT, USAF as coordinator.

This report covers work conducted from 15 November, 1965 to 15 February, 1966.

ABSTRACT

Ten commercial fuels in the jet fuel range have been examined for differences in physical properties, chemical composition, and friction/wear behavior. Viscosity, volatility, G.C. separations, sulfur, nitrogen and acidity are tabulated.

The fuels differ markedly in their friction/wear performance. Although this seems to correlate somewhat with viscosity and possibly with hydrocarbon structure, the greatest effect appears to be due to trace components in the fuel. Acid constituents appear to be most effective.

An occurrence of sticking in the fuel-control valve of operational jet engines has led to the examination of a number of commercial JP-4's from different sources. These have been found to give quite different performance in the laboratory ball-on-cylinder rig. Correlation between laboratory and field appears to be good based on the little field information available. Some of the fuels are extremely poor in lubricity.

Special lubricity additives give a marked improvement in performance in laboratory tests, including the Vickers vane pump test. Corrosion inhibitors have also been found to be effective lubricity additives. The amount of additive necessary to give substantial improvement is much less than that necessary for anti-scuff performance in the Ryder gear test. As little as 50 ppm, and probably less, alters the lubricity markedly.

Future work will concentrate on the action of lubricity additives and trace components.

I. INTRODUCTION

The goal of this work is to delineate the fuel variables that may affect friction, wear, and seizure of pumps and other equipment using jet fuel as the only fluid. In the previous two Quarterly Reports, it was reported that field and literature surveys had shown that low-viscosity, highly-refined fuels had lubrication problems, especially at higher temperatures. The cause of these problems had not been pinpointed; in fact, almost every variable had been claimed to be the critical factor: viscosity, volatility, dissolved oxygen, dissolved water, sulfur compounds, nitrogen compounds, acid compounds, aromatics, and olefins.

Data are being obtained on all these variables. Several pure hydrocarbons and ten commercial fuels have been obtained and are being analyzed to relate performance to composition. At the same time various additives and trace constituents are being added to pure fuels to determine their effect. The preliminary data showed that lubricity additives are very effective in reducing wear and friction in both laboratory rigs and a Vickers vane pump. In contrast, sulfur and nitrogen compounds were quite ineffective. There seemed to be some effect for viscosity but other factors appear to be more important.

This Quarterly Report continues the work already started and in addition presents data on additives in very low concentrations.

II. TEST FUELS AND FLUIDS

A. Viscosity and Density

The viscosities and densities of the fuels and pure hydrocarbons investigated in this work are given in Table 1. The viscosities were obtained with a Ubbelohde capillary viscometer and the densities by precision hydrometers. For all fuels and hydrocarbons the density shows an almost constant decrease of 0.00040 g/ml per °F.

The absolute viscosities (cp) of the fuels are plotted in Figure 1 and the hydrocarbons in Figure 2, using a modified ASTM chart. The ASTM chart was developed for kinematic viscosities (cs) and has been modified for absolute viscosity (cp) by relocating the vertical ordinate so that the line representing 0.4 cs becomes 0.3 cp and so on. The equation for the modified chart is thus:

$$\log \log (cp + 0.1 + k) = -m \log T + C$$

where k = 0.6 at viscosities above 1.4 cp and gradually increases at viscosities below 1.4 cp. This chart gives a relatively straight line over the range of 77-300F (25-150C).

It will be seen from Figure 1 that the jet fuels, with the exception of JP-4, have viscosities within the narrow range of 1.02-1.64 cp/100F. JP-4 is considerably lighter at 0.49 cp. Bayol 35, the white oil used as reference, is 1.84 cp. The bracketing fuels are a diesel fuel of 2.15 cp and a naphtha of 0.25 cp; these represent the extremes of the mixed fuels.

The pure hydrocarbons cover a wider range, from n-octane at 0.44 cp, to dimethanodecalin at 8.00 cp/100F. The viscosity-temperature lines of all the fuels and hydrocarbons are roughly parallel; i.e. crossovers are negligible. Thus, if one fuel is more viscous than another at one temperature, it will be more viscous at all temperatures, with only minor exceptions. The same can be expected to hold for viscosity-pressure relationships.

B. Volatility

Engler distillations of the fuels are presented in Table 2 and shown graphically in Figure 3. Gas chromotographic separation by carbon number are given in Appendix Table I. Again it can be seen that the bracketing fuels are naphtha and diesel fuel. Essentially all of the naphtha boils below the lowest boiling fraction of any other fuel; and 75% of the diesel fuel boils above the highest boiling fraction of any other fuel. The wide-cut nature of JP-4 is easily seen. Bayol 35, PW-523, 75 LN-LV, and JP-5 all have very narrow boiling ranges. AFFB-3-65 is a slightly wider cut, and RAF-173 and RAF-176 wider still, but of course, all are relatively narrow compared to JP-4. Of the jet fuels only RAF-176-64 has an appreciable amount as high as the C_{16} fraction - 3.7%. The 75 LN-LV is almost entirely C_{13} and below; AFFB-3-65 almost entirely C_{12} and below.

TABLE 1

VISCOSITY & DENSITY OF FUELS & HYDROCARBONS

	Kinematic Viscosity, cs					Density, g/ml					Absolute Viscosity, cp				
Temp. °F.	77	100	140	210	300	77	100	140*	210	300	77	100	140	210	300
Fuels															
Bayol 35	3.121	2.400	1.634	0.993	0.625	0.774	0.765	0.749	0.722	0.687	2.416	1.836	1.224	0.717	0.429
JP-5	1.835	1.486	1.102	0.728	0.494	0.799	0.790	0.774	0.747	0.711	1.466	1.174	0.853	0.544	0.351
AFFB-3-65	1.493	1.244	0.935	0.643	0.438	0.773	0.764	0.747	0.718	0.680	1.154	0.950	0.698	0.462	0.298
RAF-173-61	2.573	1.980	1.420	0.883	0.580	0.836	0.826	0.810	0.783	0.747	2.151	1.635	1.150	0.691	0.432
RAF-176-64	1.646	1.362	1.013	0.686	0.470	0.796	0.786	0.770	0.741	0.705	1.310	1.070	0.780	0.508	0.331
75 LN-LV	1.607	1.336	1.003	0.673	0.458	0.776	0.766	0.749	0.720	0.683	1.247	1.023	0.751	0.485	0.313
PW-523	1.986	1.602	1.161	0.762	0.512	0.762	0.752	0.736	0.709	0.674	1.513	1.205	0.854	0.540	0.345
JP-4	0.755	0.658	0.538	--	--	0.750	0.740	0.724	--	--	0.566	0.487	0.390	--	--
Diesel Fuel	3.418	2.608	--	1.067	0.681	0.833	0.824	0.809	0.782	0.746	2.847	2.149	--	0.834	0.508
Light Naphtha	0.429	0.386	--	--	--	0.655	0.642	--	--	--	0.281	0.248	--	--	--
Pure Hydrocarbons															
n-Octane	0.733	0.642	0.524	0.387	--	0.698	0.688	0.670	0.638	--	0.512	0.442	0.351	0.247	--
n-Nonane	0.937	0.804	0.641	0.464	--	0.713	0.703	0.686	0.655	--	0.665	0.565	0.440	0.304	--
n-Dodecane	1.828	1.496	1.117	0.740	0.503	0.746	0.736	0.720	0.691	0.656	1.364	1.101	0.804	0.511	0.330
n-Cetane	3.987	3.053	2.083	1.250	0.789	0.770	0.761	0.746	0.719	0.686	3.070	2.323	1.554	0.899	0.541
1-Hexadecene	3.528	2.736	1.911	1.163	0.745	0.778	0.770	0.754	0.727	0.693	2.745	2.107	1.441	0.845	0.516
Heptamethyl Nonane	4.262	3.240	2.187	1.300	0.782	0.781	0.773	0.758	0.732	0.699	3.329	2.504	1.658	0.952	0.547
n-Butyl Benzene	1.126	0.965	0.746	0.533	--	0.857	0.847	0.830	0.799	--	0.965	0.817	0.619	0.426	--
Decalin (cis-trans)	2.772	2.271	1.577	0.975	0.627	0.883	0.874	0.856	0.825	0.789	2.448	1.985	1.350	0.804	0.495
Tetralin	2.074	1.680	1.185	0.780	0.517	0.962	0.952	0.934	0.904	0.866	1.995	1.599	1.107	0.705	0.448
Diethylcyclohexane	1.275	1.090	0.820	0.570	0.396	0.799	0.790	0.773	0.744	0.706	1.019	0.853	0.634	0.424	0.280
Isopropyl Bicyclohexyl	9.42	6.22	3.558	1.809	1.003	0.882	0.873	0.859	0.833	0.801	8.31	5.430	3.056	1.507	0.80
Dimethano Decalin	11.49	8.06	4.687	2.284	1.223	1.003	0.993	0.976	0.946	0.911	11.52	8.00	4.575	2.160	1.114
α-Methylnaphtylene	2.655	2.045	1.414	0.869	0.561	1.013	1.004	0.981	0.958	0.921	2.690	2.053	1.387	0.832	0.517

*Interpolated

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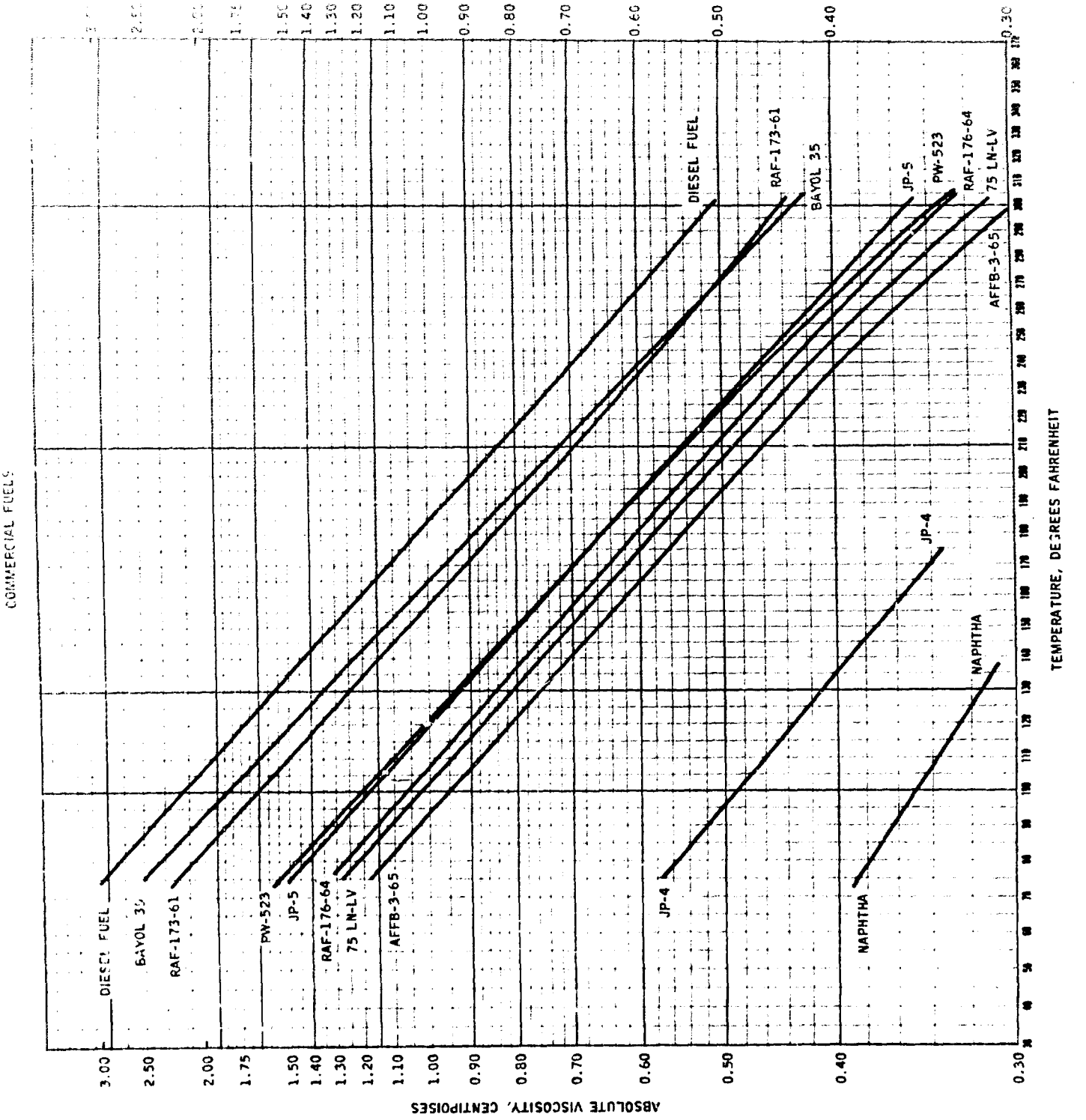

Figure 1 - Viscosity-Temperature Properties of Jet Fuels

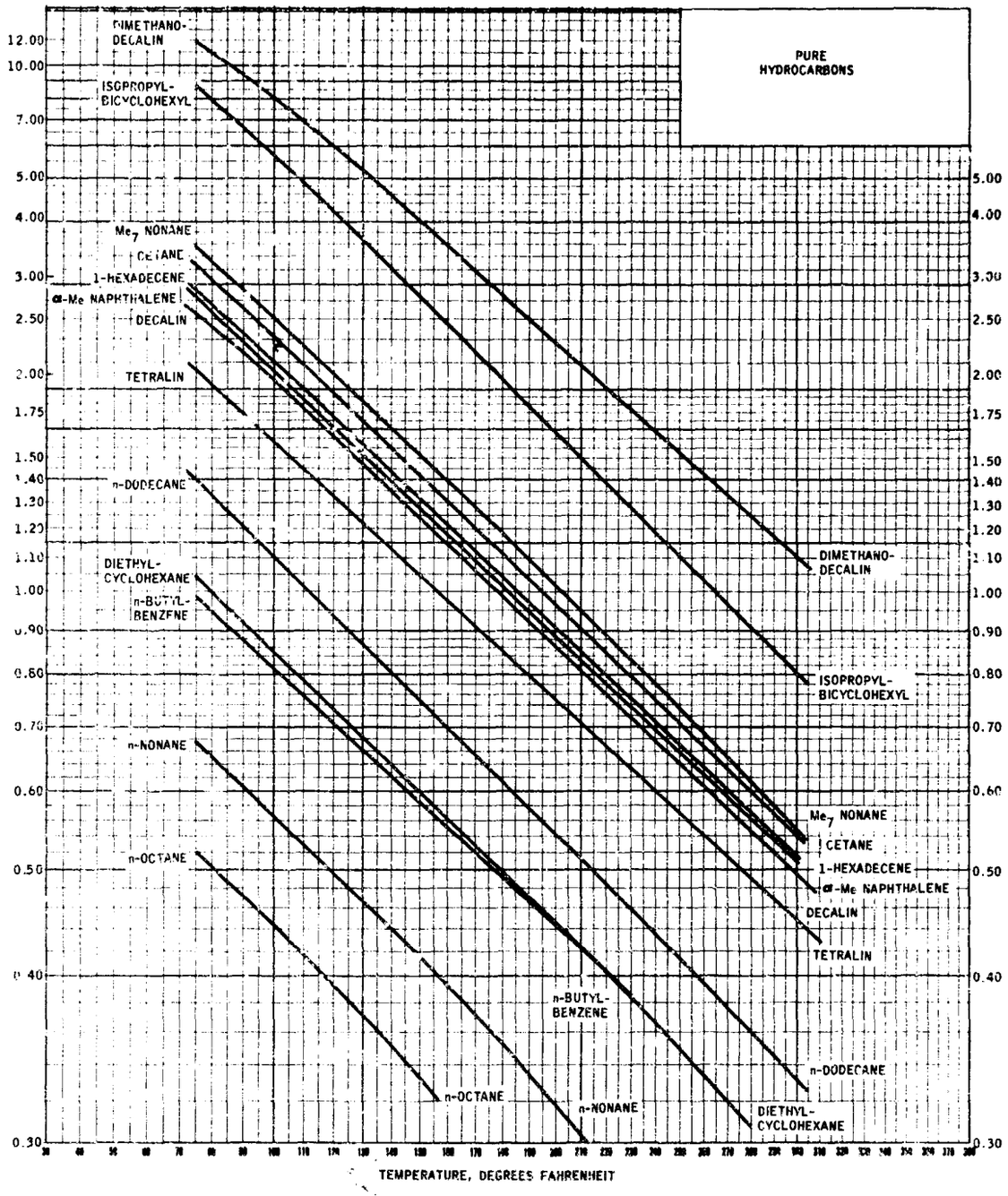

Figure 2 - Viscosity-Temperature Properties of Hydrocarbons

TABLE 2

ENGLER DISTILLATIONS OF FUELS, °F

% Dist.	Bayol 35	JP-5	RAF 173-61	RAF 176-64	AFFB-3-65	75 LN-LV	JP-4	Naphtha	Diesel	PW-523
Initial Boiling Point	402	380	372	318	312	358	156	100	402	406
5%	412	384	381	346	329	370	193	110	437	414
10%	413	388	389	348	332	371	203	114	454	416
20%	416	391	396	358	336	373	218	122	470	419
30%	421	398	405	372	343	374	230	126	483	422
40%	425	404	413	381	347	375	244	130	493	425
50%	429	407	423	392	352	376	260	135	501	428
60%	434	411	434	409	356	379	280	142	508	432
70%	439	415	444	421	363	381	306	150	522	437
80%	446	420	454	438	372	384	337	160	534	443
90%	459	429	468	456	386	390	378	173	554	454
95%	470	439	480	470	404	395	410	186	570	464
Final Boiling Point	506	469	498	482	427	422	422	205	581	482
% Recovery	98.0	98.5	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0
% Residue	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.6	1.0	1.0
% Loss	1.0	0.5	1.0	1.0	1.0	1.0	1.0	1.4	1.0	1.0

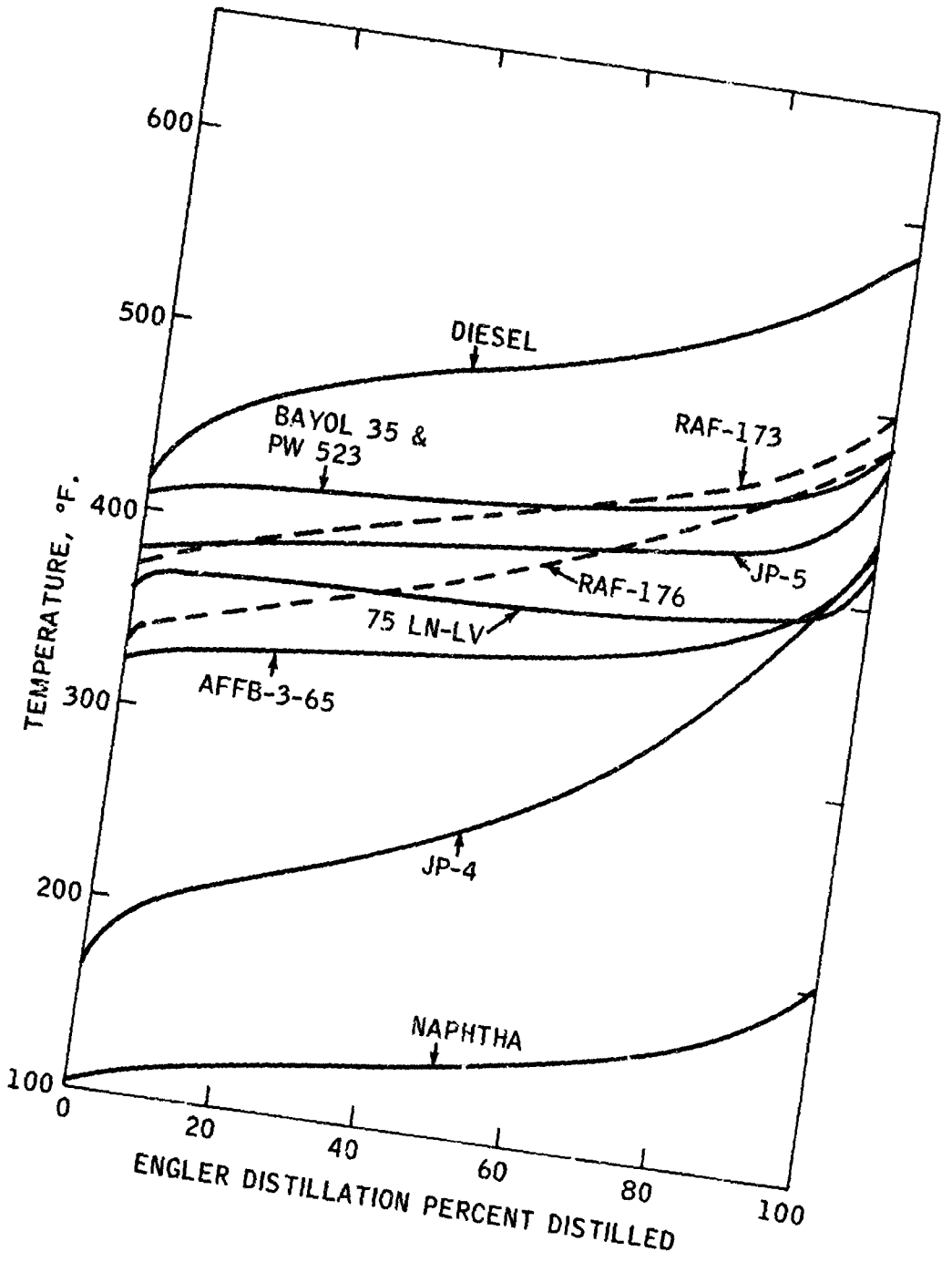

Figure 3 - Engler Distillations of Jet Fuels

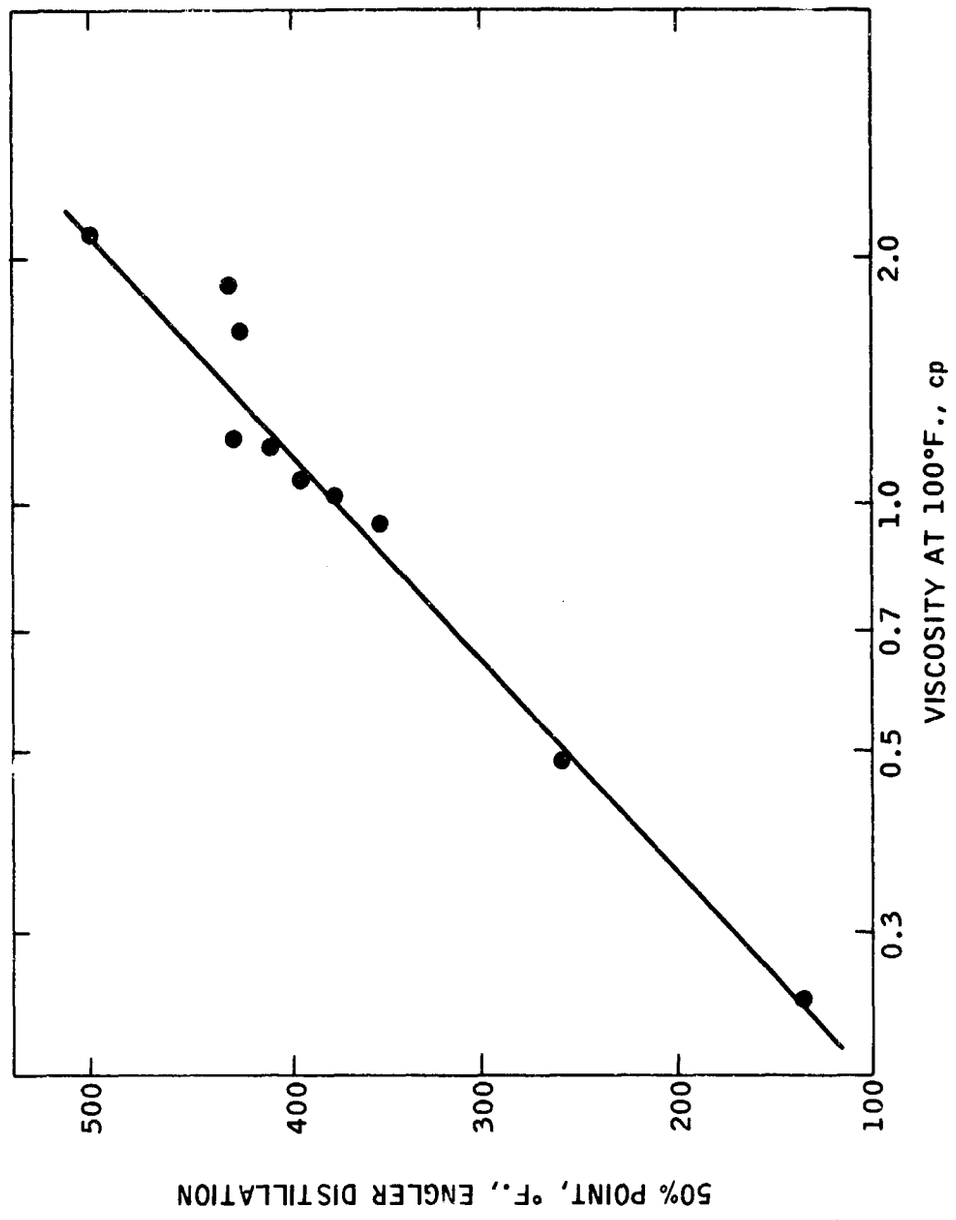

Figure 4 - Correlation Between Viscosity & Volatility

C. Trace Impurities

Table 3 lists the three most important impurities likely to influence lubricity: sulfur, nitrogen, and acidic compounds. PW-523 and Bayol 35 are very highly refined fuels and show very low S, N, and acidity. Diesel fuel is highest in all three categories, besides being the highest boiling of all fuels. RAF-176-64 is also high in sulfur and acidity; other fuels are intermediate between these two extremes.

Nitrogen contents are generally low as are the acidities. The analytical method for acidity is near its limit of accuracy at these levels, but the lubricity of the fuel could be affected by even these small amounts. As much as 25 ppm of stearic acid, for example, would give a Neut. No. of only 0.005. This will be discussed further in later sections of this report.

Aromatic contents of these fuels are being obtained.

TABLE 3

SULFUR, NITROGEN AND ACIDITY OF FUELS

	Sulfur, ppm[1]	Nitrogen, ppm[2]	Acidity Neut. No.[3]
PW-523	< 0.2	< 1	nil
Bayol 35	< 0.2	< 1	0.001
75 LN-LV	< 0.2	2	0.001
AFFB-3-65	75-80	4	0.001
RAF-173-61	29	< 1	0.003
JP-4	32-34	2	0.004
JP-5	162	< 1	nil
Naphtha	135	3	0.005
RAF-176-64	560	< 1	0.008
Diesel Fuel	2300	13	0.158

(1) Sulfur determination via Lamp method.

(2) Nitrogen determination via Kjeldahl method.

(3) mg KOH/g sample. Colorimetric titration.

III. WEAR RESULTS ON COMMERCIAL FUELS

The ten commercial fuels have been evaluated in three different wear tests: ball-on-cylinder, four-ball, and Vickers vane pump. There is a general agreement among the three test methods. Diesel fuel and RAF-176-64 consistently rate best and next best; JP-4 is considerably better than would be expected from its viscosity; PW-523 and AFFB-3-65 are generally the poorest in wear and friction. The results are discussed below:

A. Ball-on-Cylinder Tests

This test has been found to be quite sensitive to fuel behavior. Three values are measured: friction, metallic contact, and wear.

The friction shows some marked dissimilarities among fuels. A good fuel will give a steady value of friction which is at a low level; an intermediate fuel will give a ragged trace with occasional short periods of higher friction; a bad fuel will give long periods of very erratic behavior. It is impossible to represent the frictional behavior of a fuel by a single value, except in the case of the best fuels where perhaps an overall coefficient of friction can be assigned.

"Metallic contact" is a measure of the fraction of the time that the metal surfaces are in contact--measured electrically. With oils or with good fuels, this correlates well with wear. But at low loads or with fuels of erratic friction, it was found that the ball encounters stick-slip, and chatters or bounces. This gives a meaningless low value of "metallic contact". Metallic contact is therefore pertinent mostly with additive studies, where a decreasing metallic contact indicates the formation of a nonconducting surface film.

The wear of the ball has been found to be a reasonably good reflection of frictional behavior, at least for nonadditive fuels.

Tests were run on the ten fuels at loads from 30 g to 480 g, at a speed of 240 rpm (60 cm/sec) and for a 32-minute period. The wear data are presented in Table 4, where the fuels are arranged in order from bad to good. The last two columns are test run all on the same cylinder and for 64 minutes. These tests eliminate any differences due to cylinder-to-cylinder variation, which may be present in the 32-minute tests.

It will be seen that the Diesel Fuel is consistently the best. This is to be expected, for this fuel has the highest viscosity, lowest volatility, and has by far the greatest amount of sulfur, nitrogen and acidic compounds. RAF-176-64 consistently rates second. This fuel is also high in sulfur and acidic components and is higher in viscosity than the other jet fuels. Of the poorest fuels, PW-523 and 75-LN-LV are also the most highly refined, with low sulfur and acidity. AFFB-3-65 and RAF-173-61, also relatively low in trace constituents, were also poor in lubricity.

Two anomalies were noted. JP-4 was clearly better than the four jet fuels noted above and about equal to JP-5, in spite of its lower viscosity. Its trace impurities do not seem to be high enough to predict such good behavior. Bayol 35 also showed up surprisingly well, in view of its extreme purity, although it has a higher viscosity than the other jet fuels. The light naphtha is also clearly better than the four purer fuels listed above, in spite of a much lower viscosity. However, the naphtha is relatively high in sulfur, nitrogen and acidity.

TABLE 4

COMMERCIAL FUELS, BALL-ON-CYLINDER TESTS

	Wear Scar Diameter, mm										
	32 Mins					64 Mins		Vis/77F	S,	N,	Acidity
Load, g:	30	60	120	240	480	60	240	cp	ppm	ppm	mg KOH/g
PW-523	0.27	0.32	0.36	0.50	0.64	0.36	0.47	1.51	<0.2	<1	Nil
75-LN-LV	0.26	0.31	0.41	0.52	0.53	0.31	0.57	1.25	<0.2	2	0.001
AFFB-3-65	0.26	0.31	0.38	0.46	0.58	0.30	0.52	1.15	80	4	0.001
RAF-173-61	0.23	0.28	0.32	0.41	0.56	0.34	0.47	2.15	29	<1	0.003
Naphtha	0.26	0.30	0.37	0.38	0.47	0.30	0.47	0.28	135	3	0.005
JP-5	0.22	0.25	0.32	0.35	0.42	0.28	0.44	1.47	162	<1	Nil
JP-4	0.23	0.28	0.29	0.33	0.37	0.26	0.44	0.57	34	2	0.004
Bayol 35	0.21	0.25	0.29	0.35	0.42	0.24	0.46	2.42	<0.2	<1	0.001
RAF-176-64	0.17	0.20	0.25	0.28	0.30	0.22	0.34	1.31	560	<1	0.013
Diesel Fuel	0.20	0.20	0.21	0.26	0.29	0.21	0.29	2.85	2300	13	0.158

Friction generally correlated well with wear in these tests. For example, at the 60 g level, Diesel Fuel (lowest wear) gave a steady coefficient of friction of about 0.11 throughout the entire run. This contrasts with PW-523 (highest wear) which gave friction values oscillating between 0.13 and 0.29. At the 240 g level wear and friction correlated quantitatively. Again, Diesel Fuel gave a constant, steady coefficient of friction (0.13) compared to fluctuating values from 0.16 to 0.19 for PW-523.

As already mentioned, metallic contact at the 60 g level was more an indication of stick-slip and bouncing than it was of true severity of operation. At 240 g load, the film thickness was so low that metallic contact existed 100% of the time for most fuels. Only for the three best fuels--Diesel Fuel, RAF-176-64 and Bayol 35--was a decrease in metallic contact noted.

These runs establish several important points:

- Fuels differ markedly in their friction and wear behavior.
- The differences are apparently more a function of trace impurities than bulk viscosity, but this is not entirely clear-cut.
- Frictional behavior can be determined from the wear scar for nonadditive fuels.
- The ball-on-cylinder machine is a useful laboratory device for assessing frictional behavior of jet fuels.

B. Four-Ball Tests

The four-ball data obtained during previous periods as documented in Quarterly Progress Reports No. 1 and No. 2 have substantiated that, with a few rare exceptions, the slope of the line representing the normal wear region on a log-log plot of wear scar diameter vs. time is 0.25. This is a mathematical consequence if the wear volume per unit time is a constant. The test conditions of previous experiments covered loads ranging from 5 to 50 Kg, speeds from 600 to 1800 rpm, and time from a few seconds to several thousand minutes. At the higher loads and speeds, the test results were sometimes erratic. For further wear experiments the following test conditions have been standardized to minimize the total number of tests:

a. Test loads and speed have been chosen to be 10 Kg and 1200 rpm, respectively.

b. The equilibrium wear scar requires excessively long test durations for low viscosity fluids and is therefore not pursued.

c. Five test durations, 15 sec., 1 min., 4 min., 15 min., and 1 hr., have been chosen to define the normal wear region and to get some indication of the level of initial wear.

d. For less extensive tests three test durations, 4 min., 15 min., and 1 hr. have been chosen for determining the normal wear region.

e. A test temperature of 97 F (36 C) was adopted as a convenient temperature--somewhat above ambient--that could be maintained in spite of frictional heating. This particular temperature was chosen because it formed the base of another part of the program: n-heptane has the same viscosity at 97 F as JP-5 at 300 F.

Figures 5 and 6 are log plots of WSD vs. time and show the relative performance of the ten commercial fuels. The data are summarized in Table 5, which gives the wear rate (cu mm/min), the corresponding WSD at 60 minutes, and the viscosity and trace impurity contents of the fuels.

TABLE 5

FOUR-BALL WEAR TESTS

10 Kg, 1200 rpm, 97 F

Fuel	Wear Rate $Min^3/Min \times 10^4$	Calc WSD at 60 Min	Vis/97F, Cp	Neut No. Mg KOH/g	S, ppm	N, ppm
Naphtha	11.1	1.44	0.25	0.005	135	3
AFFB-3-65	3.0	1.04	0.98	0.001	80	4
PW-523	1.3	0.86	1.21	Nil	<0.2	<1
RAF-173-61	1.1	0.81	1.70	0.003	29	<1
Bayol 35	1.0	0.80	1.88	0.001	<0.2	<1
75-LN-LV	0.61	0.70	1.04	0.001	<0.2	2
JP-5	0.61	0.70	1.21	Nil	162	<1
JP-4	0.37	0.62	0.50	0.004	34	2
RAF-176-64	0.33	0.61	1.09	0.013	560	<1
Diesel Fuel	0.18	0.52	2.18	0.158	2300	13

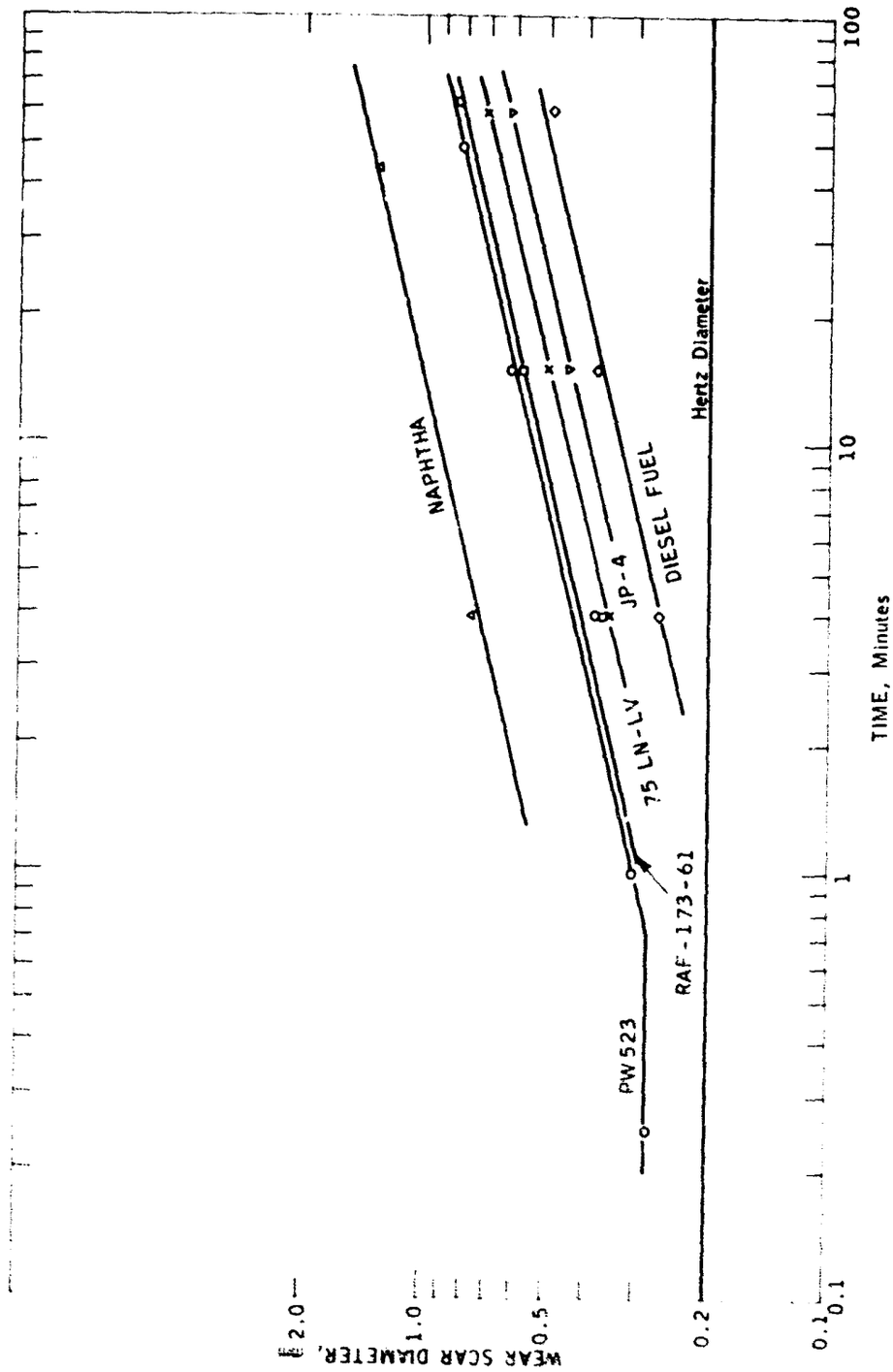

Figure 5 - Four-Ball Wear Tests on Commercial Fuels - I

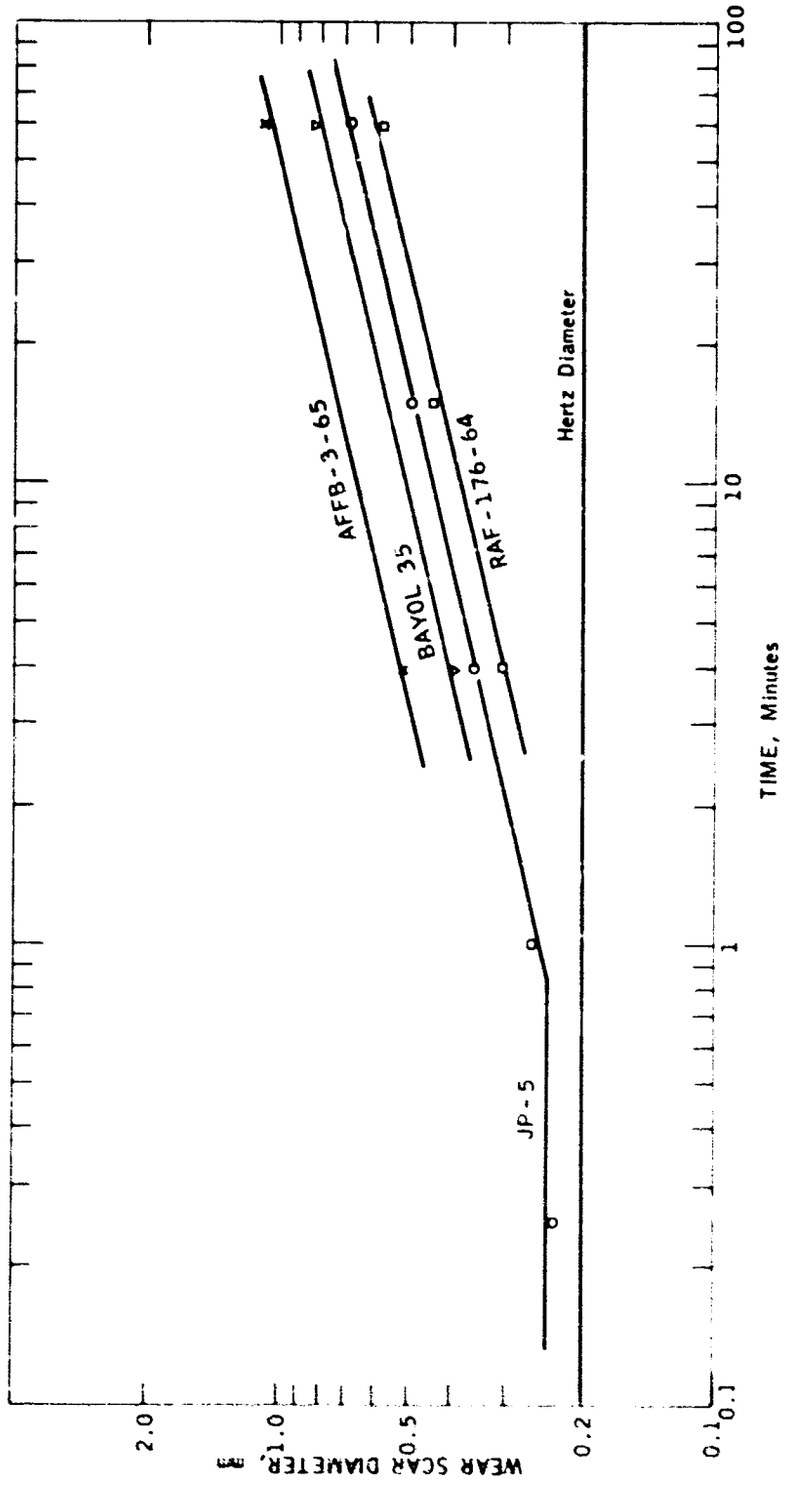

Figure 6 - Four-Ball Wear Tests on Commercial Fuels - II

Diesel fuel was again best, as would be expected. and RAF-176-64 again second best. PW-523, 75-LN-LV, AFFB-3-65 and RAF-173-61 all gave relatively high wear. Again, JP-4 outperformed all other jet fuels in spite of low viscosity, possibly because its wide-cut nature permits a relatively large amount of high-lubricity compounds.

Unlike in the ball-on-cylinder tests, naphtha in the four-ball test was by far the poorest, possibly because its very low viscosity is more critical in this test.

Bayol 35 was also relatively poor compared to the ball-on-cylinder results, being in part little better than PW-523. AFFB-3-65 was also unaccountably worse than expected.

The differences in the behavior of these two test methods and the anomalous behavior of certain fuels will be examined more closely in future work.

C. Vickers Vane Pump Tests

1. Commercial Fuels Show Marked Differences in Pump Wear

Of the ten commercial fuels, nine have been tested in the Vickers vane pump. The naphtha was found to be too low in viscosity, giving essentially no output. Test data are shown in Table 6. As in the laboratory rigs, these fuels gave a very different pump wear. For highly-refined fuels, such as PW-523 and Bayol 35, severe wear occurred. The total wear amounted to approximately 5000 mg. For some other fuels like RAF-176-64 and diesel fuel, the wear was very mild, <100 mg. It was noted during the tests that for fuels giving low wear (<200 mg weight loss), a visible deposited film was coated on the rubbing area of contact and might account for the wear protection. These deposited materials were collected for I.R. analyses. The results will be discussed in the subsequent section.

The effect of temperature on the severity of wear is not clearly defined in these data. For fuels giving severe wear, it appears that wear generally increases when going from 90 F to 125 F. In the case of PW-523 and AFFB-3-65, the higher temperature runs had to be terminated because of excessive wear and low volumetric efficiency. However, for those fuels giving mild wear such as RAF-176-64, 75-LN-LV or diesel fuel, the increase of temperature seems to further reduce the wear. This indicates that these fuels might contain trace components and that the antiwear effect of these becomes more pronounced at a higher temperature. The abrupt increase of wear by increasing the sump temperature from 90 F to 125 F indicates a sharp transition from mild to severe wear.

JP-4, because of its relatively low viscosity, could only be tested at a slightly lower pressure (300 psi) and lower sump temperature; (83 F) otherwise volumetric efficiency was nearly zero. However, in comparison with Bayol 35 under even milder conditions (Figure 10, Quarterly Report No. 1), JP-4 gave less ring wear and vane wear although its viscosity is considerably lower than Bayol 35 (0.54 vs. 2.06 cp). This, again, indicates that viscosity is not the governing factor in wear severity in the Vickers pump.

2. Correlation between Trace Impurities and Pump Wear Is Indicated

The effect of viscosity and trace components in fuels on pump wear was investigated by analyzing the test data by means of Spearman's rank correlation method. Each fuel is ranked as 1, 2, 3 . . . for each variable and the variables are then

TABLE 6

VICKERS PUMP TESTS FOR VARIOUS FUELS

	Bayol 35	JP-5		PW-523		AFFB-3-65		RAF 176-64		RAF-473-61		75-LN-LV		Diesel Fuel		JP-4
Pressure, psig	350[a]	350	350	350	350[b]	350	330[c]	350	300	350	350[d]	350	350	350	350	300
Sump Temp., °F	90	90	124	90	125	90	125	90	125	90	125	90	125	90	125	83
Outlet Temp., °F	115	94	134	110	146	106	145	96	136	98	144	104	136	94	136	104
Pumping Rate, gpm	0.43	0.77	0.55	0.46	0.29	0.47	0.33	0.87	0.32	103	0.38	0.67	0.46	1.10	0.77	0.32
Vol. Eff., %	24	43	30	26	16	26	18	48	18	57	16	37	26	61	43	16
Wear, mg:																
Wt. Loss of Vanes	204	85	11	100	19	661	19	4	0[e]	31	294	50	0[e]	0[e]	6	3
Wt. Loss of Ring	5150	561	1119	4844	147	3656	104	67	39	235	4240	200	127	4	4	157
Total Wt. Loss	5354	646	1130	4944	166	4317	123	71	39	266	4534	250	127	4	10	160
Surface Roughness, CLA, μ":																
Vanes, Initial	3.9	15	14	18	17	24	24	20	16	23	14	20	21	14	18	19
Final	96	103	10	82	75	>200	96	17	14	123	171	97	20	17	25	10
Ring, Initial	15.8	16	16	18	16	16	28	17	16	10	8	9	12	9	12	10
Final	67	22	6	41	17	97	36	14	9	88	81	19	9	6	6	5
Viscosity, cs																
Before Test, @ 100°F	2.39	1.49	-	1.60	-	1.24	-	1.36	-	1.98	-	1.32	-	2.6	-	0.76 @ 77°F
@ 210°F	1.00	0.73	0.73	0.76	0.77	0.64	0.65	0.69	0.71	0.88	0.89	0.67	0.68	1.07	1.06	-
After Test, @ 100°F	2.40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.80 @ 77°F
@ 210°F	-	0.73	0.73	0.77	-	0.65	-	0.71	0.71	0.89	0.89	0.68	0.68	1.06	1.07	-
Neut. No. mg KOH/gm:																
Before Test	0.001	0.002	0.001	0	0.004	0.001	0	0.013	0.007	0.003	0.002	0.001	0.005	0.158	0.160	0.004
After Test	-	0.001	0.008	0.004	-	0	-	0.007	0.008	0.002	0.005	0.005	0.006	0.160	0.203	0.003

(a) Run at 125°F sump temperature was stopped at 15 minutes due to excessively low volumetric efficiency. Ring wear was 122 mg and vane wear was 14 mg.

(b) Run was stopped at 20 minutes due to excessively low volumetric efficiency.

(c) Run was stopped at 45 minutes due to excessively low volumetric efficiency.

(d) Run was stopped at 21 hours due to excessively low volumetric efficiency.

(e) Slight weight gain.

compared. The coefficient of correlation γ_s, can be computed for two variables which are hypothesized to be correlated. The calculated coefficient, γ_s, is compared with the given acceptance limits to determine the significant evidence at a certain confidence level. This analysis is a rank randomization test. It is used here to detect whether the variation of wear is directionally consistent with that of viscosity or content of trace components. The equation for computation and the computed results are shown in Table 7.

a. Viscosity

The viscosity of the fuels after each test was checked and showed no appreciable change. Values of viscosity at any specified temperature in pump tests were therefore interpolated from the analytical results given in Table 6. As shown in Table 7, under these test conditions, no significant correlation is detected between the severity of wear and the viscosity at the sump temperature. A further analysis was made using the viscosity at the outlet temperature which is closer to the bulk fuel temperature inside the pump. The combined test data at two sump temperatures, exclusing those with very short duration, are tabulated in Table 8. The result still fails to show a correlation between the viscosity and wear. There is, of course, a correlation between viscosity and volumetric efficiency. Excluding these runs with severe wear ($<$3000 mg ring wear) which caused the excessive loss of volumetric efficiency, a linear relationship between the viscosity and volumetric efficiency is indicated in Figure 7. The linear correlation coefficient was computed to be 0.91, showing a significant correlation at 99% confidence level. The line of regression was thus determined and is also shown in Figure 7.

b. Sulfur Content

There is a significant correlation between sulfur content and anti-wear level for both the 90 F and 125 F tests. Bayol 35 and PW-523 had negligible sulfur contents (less than 0.2 ppm) and the highest wear. Diesel fuel (2300 ppm) and RAF-176-64 (560 ppm) had the highest sulfur content and the lowest wear. Inasmuch as sulfur compounds are well known EP agents (that is, they inhibit scuffing wear), it appears that unsatisfactory performance in the Vickers vane pump is a scuffing phenomenon. It need not be wholly related to sulfur content, however, because a high sulfur is generally indicative of high trace impurities of all kinds.

c. Acidity

There is also a correlation between anti-wear performance and acidity (neutralization number). This is further borne out in the additive studies where trace amounts of acidic additives can have a pronounced anti-friction effect in the ball-on-cylinder device. On the other hand, the acidity of many of the fuels is so low that the small differences may be within the experimental error. Acidity increased only slightly in any of the tests, indicating that oxidation was negligible.

3. Friction in Pump Varies for Different Fuels

A difference of pump outlet temperature for various fuels tested at the same sump temperature and pressure was evident. The variation of the temperature gradient between the inlet and outlet of the pump indicates the difference of

TABLE 7

RANK CORRELATION FOR TEST DATA FROM VICKERS PUMP TESTS

Acceptance Limits: $\gamma_{s,0.01} = 0.833$, $\gamma_{s,\ 0.05} = 0.64$

	Sump Temperature °F	$*\gamma_s$	Evidence of Significance
Wear vs. Viscosity	90	0.12	No
Wear vs. Viscosity	125	0.03	No
Wear vs. ppm S	90	0.74	Significant at 95% A.L.
Wear vs. ppm S	125	0.76	Significant at 95% A.L.
Wear vs. Neut. No.	90	0.81	Significant at 95% A.L.

$$* \gamma_s = 1 - \frac{6}{n(n^2-1)} \sum d^2$$

where d = the difference of numerical ranks of two corresponding variables,

n = number of fuels ranked.

(G. W. Snedecor's "Statistical Methods," p. 164)

TABLE 8

VISCOSITY VS VOLUMETRIC EFFICIENCY AND WEAR

	Outlet Temperature °F	Viscosity cp	Vol. Efficiency %	Wear, mg	
				Ring	Vane
Diesel Fuel	94	2.30	61	4	0
RAF-173-61	103	1.60	57	235	31
Bayol 35	115	1.55	24	5150	204
Diesel Fuel	136	1.36	43		6
JP-5	94	1.23	43	561	85
RAF-173-61	144	1.10	16	4240	294
RAF-176-64	96	1.10	48	39	0
PW-523	110	1.10	26	4944	100
75 LN-LV	104	0.91	37	200	50
AFFB-3-65	106	0.90	26	3656	661
JP-5	134	0.88	30	1119	11
75 LN-LV	136	0.78	26	127	0
RAF-176-64	142	0.77	18	39	0
JP-4	104	0.47	18	157	3

Spearman Rank Correlation

Acceptance Limit: $\gamma_{s,\ 0.05} = 0.456$

$\gamma_{s,\ 0.01} = 0.645$

Viscosity vs. Ring Wear, $\gamma_s = 0.11$, No Correlation.

Viscosity vs. Vane Wear, $\gamma_s = 0.25$, No Correlation.

Viscosity vs. Vol. Efficiency, $\gamma_s = 0.62$, Significant at 95% A.L.

FIGURE 1

VISCOSITY VS. VOLUMETRIC EFFICIENCY

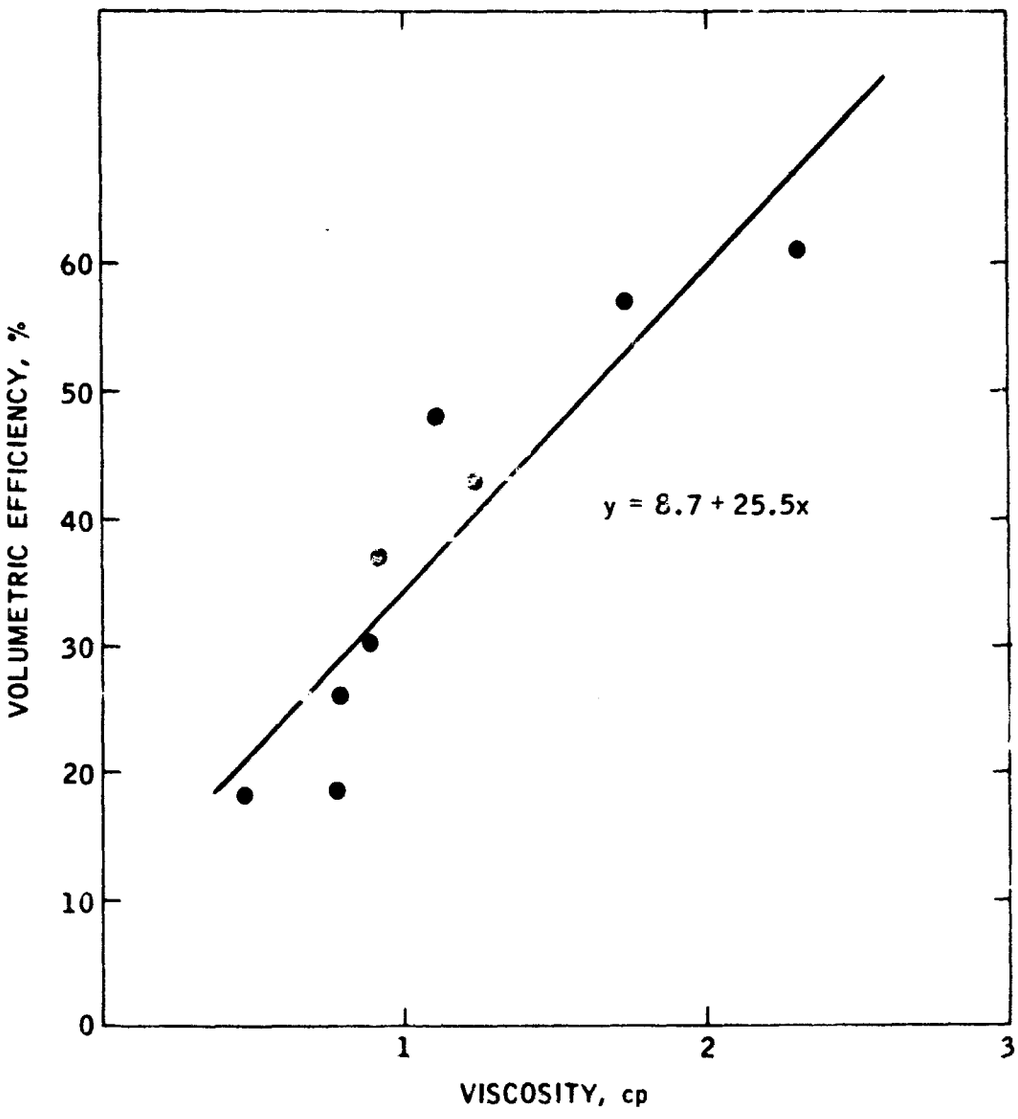

Figure 7 - Viscosity vs. Volumetric Efficiency

friction for various fuels in pump operation. The power loss (ΔP_F) due to friction was estimated by an energy balance using such test data as the sump temperature (T_s), outlet temperature (T_o), pumping pressure (P), fuel density (ρ), pumping rate (V):

frictional power loss = heat absorbed by fluid per unit time + rate of heat loss to surroundings

$$\Delta P_F = V \left[C_p \rho (T_o - T_s) J - 144 P \right] + J (h_c + h_r) A (T_o - T_a) \qquad (1)$$

C_p is the specific heat of various fuels and is obtained from the generalized chart on page 93 of Maxwell's "Data Book on Hydrocarbons."

J is the heat-energy conversion factor.

$(h_c + h_r)$ is defined as the combined coefficient for convection and radiation (Perry's Handbook of Chemical Engineering, Third Edition, p. 474).

A is the exposed area for heat loss.

T_a is the ambient temperature.

The friction force, F, can then be evaluated from

$$F = \frac{\Delta P_F}{U} \qquad (2)$$

where U is the linear velocity of rotation. The load of the vanes on the ring surface is mainly from the back pressure of the discharged fuel. Since in the discharge cycle the pressure is counterbalanced, only the six vanes in the suction cycle are loaded. Based on this information, the total load and then the coefficient of friction can be evaluated.

These computed values of friction are tabulated in Table 9. The coefficient of friction ranges from 0.05 to 0.41. These results indicate that the friction is generally high when severe wear occurs. However, there are exceptions. 75 LN-LV fuel and JP-4, for instance, gave a friction coefficient $\geq$ 0.3. The wear for both fuels was rather low. It appears that the anti-scuffing effect prevails as long as a surface protective film is present on the rubbing area, but this film is not necessarily effective in reducing friction.

There seems to be a general tendency for friction to increase at a higher temperature for most fuels with the one exception of 75 LV-LN which had lower friction at the higher temperature. It is interesting to note that this same effect was observed for additive fuels, as noted later. This again indicates that the frictional behavior of fuels containing additives is quite unpredictable, even though they all show a pronounced anti-wear effect.

4. The Ring Surface Softened after Severe Wear

The two rubbing surfaces of the pump cartridge are made of deep-hardened alloys with a hardness of 60 Rockwell C and a high resistance to wear. The vane

TABLE 9

FRICTION DATA FOR VICKERS PUMP TESTS

p = 350 psig

	Sump Temperature °F	Power Loss Due to Friction ft-lb/sec	Friction lb	Coefficient of Friction (f)
Diesel Fuel	90	84.0	7.2	0.07
	125	251.0	21.6	0.22
Bayol 35	90	460.7	39.6	0.41
RAF-173-61	90	260.0	22.3	0.23
	125	276.0	23.8	0.25
PW-523	90	395.7	34.0	0.35
JP-5	90	59.0	5.1	0.05
	125	192.0	18.3	0.19
RAF-176-64	90	146.2	12.5	0.13
	125	210.0	20.0	0.21
75 LN-LV	90	367.4	31.6	0.32
	125	165.0	16.0	0.17
AFFB-3-65	90	289.2	24.8	0.26
JP-4	*84	287.4	24.7	0.30

* At 300 psig pressure.

is made of a molybdenum base tool steel having a high resistance to softening at high temperature. The ring was made of a deep hardened bearing steel having a low resistance to softening at high temperature (>300°F.). The hardness of the wear surface of the vane was measured after the test and found to have undergone little change. In contrast, a decided change in the hardness of the rings was noted. It was also found that the hardness at various spots on the wear surface varied over a wide range. A macro etching procedure was employed to identify the variation of hardness on the metal surface, using a Nital solution (2% HNO_3 in alcohol). As an illustration, a micrograph of a segment of the etched ring from a pump test using AFFB-3-65 fuel is shown in Figure 8. The dark area is the softened region, having a 40-52 Rockwell C hardness, while the light area shows only a small change of hardness (57-60 Rockwell C). The reason for this non-uniformity of hardness is unknown. The values of hardness for wear surfaces of rings from pump tests using various fuels are listed in Table 10. It is interesting that the severity of wear can be estimated from the lowest value of hardness: A ring surface softened to 45 Rockwell C or less indicates severe wear; one softened to 55 Rockwell C indicates mild wear. When there was very little wear (e.g., diesel fuel tested at 90°F. sump temperature), the hardness of the ring was practically unchanged. It is known that this alloy does not soften appreciably below a temperature of 300°F., which is considerably higher than the bulk fuel temperature in any tests. This is good evidence that a local high temperature on the rubbing surfaces was developed due to the metal-to-metal contact. It is therefore postulated that in severe wear the ring surface was softened by the high local temperature and then scoring occurred due to the difference of hardness between the ring and the vane which could retain its hardness at such a high temperature. The presence of a surface protective film minimized the metal-to-metal contact, so that the ring was softened to a lesser extent. This might contribute to the reduction of wear.

5. Jet Fuel Additives Show Pronounced Anti-Wear Effect

Three jet fuel additives were tested in the Vickers vane pump at 0.1% concentration (by weight) in Bayol 35. The test conditions were the same as or at a higher temperature than that under which severe wear occurred with Bayol 35 alone. All showed an anti-wear effect, as shown in Table 11.

In comparison, ER-2 and ER-3 are somewhat more effective than ER-1 in that ER-1 gave higher initial wear and roughened the rubbing surfaces. A deposited film was observed on the contact surfaces of the vanes for all these additive fuels. This could account for their anti-wear effect.

D. Analysis of Wear Deposit

In many of the tests made in the Vickers vane pump, a dark brown-black deposit was found on the vane faces and ring. This was found when running straight fuels as well as anti-wear additive-containing fuels. This deposit was generally quite hard and varnish-like and relatively insoluble in common organic solvents. The deposit, which was carefully removed from the hard metal surface with a razor blade, totaled approximately 1-10 mg. Due to the small sample size, the deposit was scraped directly into a vial from which a KBr pellet was formed for infrared analysis. Other techniques, such as ATR-IR and solution methods, were found unsatisfactory.

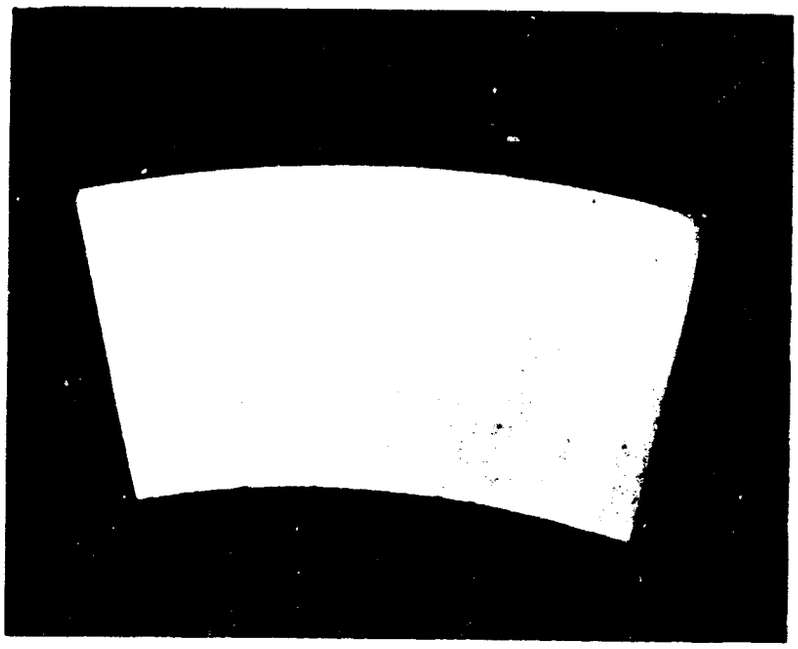

Figure 8 - Etched Ring Segment From a Pump Test With AFFB-3-65 (5X)

TABLE 10

HARDNESS OF RINGS AFTER PUMP TESTS

Fuel Used	Sump Temperature, °F.	Hardness, Rockwell C		Ring Wear mg
		Dark Area*	Light Area*	
Bayol 35	90	44-47	56-60	5150
PW-523	90	39-50	56-59	4944
RAF-173-61	125	44-50	55-60	4240
AFFB	90	44-52.5	5[illegible]5-60	3656
JP-5	125	44-51	53-57.5	1119
JP-5	90	51-56	57-59	561
RAF-173-61	90	51-56	58-59	235
75 LN-LV	90	54-6[illegible] *		200
JP-4	84	54-59.5**		157
75 LN-LV	125	55-59.5**		127
RAF-176-64	90	53-[illegible]	58.5-59	67
Diesel Fuel	90	57-59**		4
Diesel Fuel	125	55-59.5**		4
New Ring	-	58-59.5**		-

* Etched area.

** Dark and light areas are not distinguishable.

FF[illegible]:gde
3/7/66

TABLE 11

VICKERS VANE PUMP TESTS
WITH ADDITIVE FUELS

	Bayol 35 (Base Fuel)	0.1% ER 1 in Bayol 35		0.1% ER 2 in Bayol 35		0.1% ER 3 in Bayol 35	
Pressure, psig	350	350	350	350	350	350	330
Sump Temp., °F.	90	90	125	90	125	90	125
Outlet Temp., °F.	115	96	134	102	130	102	136
Pumping Rate, gpm	0.43	1.05	0.42	0.74	0.82	1.00	0.33
Vol. Eff., %	24	58	23	41	46	56	18
Wear, mg							
Wt. loss of vanes	204	0*	22	0	6	0*	0*
Wt. loss of ring	5150	135	40	21	21	13	0
Total wt. loss	5354	135	61	21	27	13	0
Surface Roughness, CLA, μ"							
Vanes, initial	3.9	16	27	19	21	20	24
final	96	18	118	23	16	20	22
Ring, initial	16	13	10	11	17	13	10
final	67	21	48	17	9	7	6
Coefficient of Friction	0.41	0.16	0.16	0.29	0.10	0.38	0.13

* Slight weight gain.

1. Fuels

The straight fuels can be divided into two groups with regard to their tendency to form these deposits. The more highly refined materials, AFFE-3-65, RAF-173-61, PW-523, and Bayol 35 show no significant coating on the pump parts. The remainder, JP-4, diesel fuel, RAF-176-64, 75LV-LV, and JP-5 did leave deposits which were analyzed via IR spectrospcopy. It is noteworthy that the fuels which failed to show a deposit were also the fuels giving the highest wear.

With the exception of the diesel fuel, the spectra of the deposits for the fuels indicated basically the same results, namely, that carboxylate ion was present in all cases.

a. JP-4, RAF-176-64, JP-5

The spectra show the presence of hydrocarbon from C-H stretching mode at 3.4μ; the double peaks at 6.4 and 7.1μ are indicative of carboxylate ion absorption; there is little evidence of free acid; a major peak at~9.5 is thought to be due to the presence of dirt or dust in the system; there is also some indication of the occurrence of hydrocarbon cracking.

b. 75LN-LV

At 90°F. sump temperature there is evidence of acid carbonyl at 5.8μ; otherwise, the spectrum is similar to the foregoing analyses. In the higher temperature run (125°F. sump temperature), the acid function has disappeared and the spectrum is quite similar to the three fuels mentioned above.

c. Diesel Fuel

The spectrum for this material does not show the presence of any functional groups. The deposit was not very heavy, hence, the spectrum is poorly resolved.

2. Additive-Containing Fuels

Various jet fuel anti-wear additives were evaluated in the Vickers vane pump as 0.1% or 1.0% solutions in Bayol 35. In addition to the five additives already included in the program, a test was made using a 1% solution of bright stock in Bayol 35. Bright stock is a highly refined paraffinic oil with a viscosity of 1000 cs at 77°F.

a. 1% Bright Stock in Bayol 35

The deposit remaining on the pump parts after this run yielded an IR spectrum similar to that of a saturated hydrocarbon oil with a well-defined peak at 3.4μ (C-H stretching) and a peak at 13.9 indicative of a long chain hydrocarbon. This was substantiated by large methyl and methylene absorption in the 6.9-7.3 region. There was also evidence of some oxidation, as shown by the bands at 5.7, 5.8, and 6.2μ due to ester, acid, and carboxylate ion, respectively. This spectrum is clearer than others due to the fact that the deposit was evaporated on a salt plate rather than run as a KBr pellet. The relatively large amount of sample and its solubility in CCl_4 allowed such a determination.

The anti-wear additives were all run as 0.1% solutions in Bayol 35.

b. Zn DDP and TCP

These two common anti-wear agents failed to yield a large deposit and the KBr-IR spectra are poorly defined. The only obvious functionality present is the C-H stretching mode and a broad absorption at 9-10μ which can be ascribed to phosphate ion and degradation products thereof.

c. ER 3

The infrared spectrum of the deposit found after using this material strongly indicated the presence of organic ester, acid, and carboxylate ion. The hydrocarbon modes at 3.4 and 13.9μ were also present.

d. ER 2

The spectra obtained with this material are somewhat unusual in that they indicate a high concentration of methyl groups similar to polyisobutylene. The more predictable soap formation is also shown, along with carboxylic ester absorption. The presence of a high methyl content does not agree with the probable chemical constitution of this additive.

e. ER 1

Due to a relatively small deposit, the spectrum of this material is poorly defined with the major absorption from C-H stretching at 3.4μ. There is a broad band from 5.8 to 6.6μ, indicating the possible presence of oxygenated species but this assignment is uncertain.

It appears clear that the main function of these anti-wear additives is to provide a polar component which can be adsorbed on the metal surface and which can react with the surface to form a protective film or is degraded to a species which can then react to form a protective film. In the case of the straight fuels, those materials possessing few polar constituents are more prone to wear, while the fuels containing a greater amount of polar bodies are able to protect the metal surfaces by depositing a protective film or by having a constituent molecule degraded on the surface to form this film. In this sense these latter fuels and additive-containing fuels accomplish the same end, but the speed and degree to which the protective film is formed is undoubtedly concentration dependent. Hence, the additive-containing fuels would be superior in reducing wear.

E. Influence of Polar Species on the Lubricity of Jet Fuels

The data of the preceding three sections indicate that the presence of minute amounts of polar constituents in hydrocarbon fuels favorably affect their lubricity properties. The term, "polar constituents," is intended to cover almost all species present in a blend aside from paraffinic and naphthenic entities. Thus, compounds containing hetero atoms (e.g., S, N, O) as well as olefinic and aromatic materials are included in this category.

In highly refined fuels this "polar" component is quite small, usually less than 1%. The problem of investigating the effect of such materials on fuel lubricity can be considered in the following manner. First, the polar component can be removed from the fuel and the lubricity properties of the treated and untreated fuels compared to determine the importance of such a treatment. Second, in the

event that a significant difference is uncovered for the non-polar fuel, the actual isolation and identification of the polar compounds and/or the blending of suitable polar materials into treated fuel will allow a direct determination of the fuel lubricity components.

One obvious separation method is percolation of the fuel through suitable adsorbents, such as silica gel or "Florosil." Not only can the fuel be purified of polar components but such components can be recovered by elution with various solvents.

In the experiments done to date, the hydrocarbon was passed through a three-foot high, one-inch I.D. column packed with W. R. Grace silica gel. The column was packed dry and quickly covered with the hydrocarbon to be treated. Percolation was continued until one liter had been added to the column. This column-treated material was used in various friction and wear tests, after which the polar component adsorbed at the top of the column was eluted with a 50% methanol-50% acetone solution. The acetone-methanol was driven off under vacuum and mild heating to free the "polar component" fraction.

In the initial experiments in this series, the performance of diesel fuel was evaluated. The diesel fuel has been shown to contain the highest amount of sulfur and nitrogen of the fuels to be tested in this program and is also highest in acidity.

After silica gel percolation, analyses were made to determine the effect of the treatment on the chemical composition of the fuel. These include sulfur and nitrogen content and infrared and NMR spectra of the original material, the percolated fuel, and the polar material desorbed from the column.

The table below shows the effect of column treatment on sulfur and nitrogen content:

Silica Gel Removes Sulfur and Nitrogen Compounds

	Original Diesel Fuel	Silica Gel-Treated Diesel Fuel	Column Eluate
Sulfur Content, ppm	2,300	0.6	15,700
Nitrogen Content, ppm	14	<1	18

The above data indicate that the sulfur has been effectively concentrated in the polar component (a sevenfold concentration of the original fuel would yield a value of 16,000 ppm in the eluate if it were completely removed). In the case of nitrogen, the situation is not clear since the method of nitrogen analysis also utilized a column treatment to concentrate the nitrogen. These analyses are being repeated. However, the analyses do indicate that the more polar nitrogen compounds have been removed from the treated fuel.

An accurate material balance on the diesel fuel has not been obtained due to experimental difficulties. The method of evaporating the eluting solvent from the polar component may have resulted in the loss of some of the lighter materials in this fraction. Future experiments will be designed so as to avoid this difficulty.

Ball-on-cylinder tests have been run on the original diesel fuel and each of the two fractions.

Table 12

Ball-on-Cylinder Tests
(240 rpm, 32 min.)

Treatment	Load, g:	Coefficient of Friction 60	240	1000	Wear Scar Diameter, mm 60	240	1000
None		0.12	0.13	0.14	0.21	0.25	0.30
Silica-Gel Extracted		0.22	0.20	0.16	0.24	0.30	0.42
Eluate		0.08	0.13	0.12	0.36	0.47	0.48

The results are somewhat surprising. The friction results are normal, with the polar eluate giving less friction than the whole fuel and the purified fraction giving more friction and very erratic traces. But, the wear scars do not show a similar trend: Both the extracted material and the eluate gave more wear than the whole fuel. One reasonable explanation of this is as follows: The absence of polar impurities in the extracted portion causes high friction and wear; the concentration of these polar impurities in the eluate gives low friction because the impurities react with the surface to give an easily smearable layer; this layer is easily worn away, however, giving higher wear. This is reinforced by data on the metallic contact which was considerably lower for the column eluate than the whole fuel, both at 60 and 240 g loads. This indicates some kind of surface reaction which may account for the higher wear. The behavior of the extract to give low friction but higher wear is similar to that of certain additives in JP-4, as will be discussed in Section IV.

The second experiment in the series involved the silica-gel treatment of n-cetane followed by tests similar to those described above. The cetane was of high purity (Humphrey Chemical Company, 97.5% C_{16}) and was passed through the same column described previously. (An intense yellow band developed at the top of the column during treatment.) The first 100 cc of treated cetane were immediately run in the ball-on-cylinder machine; the rest of the cetane was taken off using n-pentane, and finally the yellow band which had developed at the top of the column was eluted with the 50% acetone-50% methanol solution. The yield of "polar" component in the cetane was approximately 0.8%. The yellow column eluate was concentrated and separated into two layers. Both samples were analyzed via their UV spectra. The top layer was identified as a primarily long chain ketone, similar to 2-methyl-3 decanone, the longest chain ketone of known spectrum. It is quite conceivable that this material is a C_{16} ketone, an intermediate in oxidative breakdown of n-cetane. The lower layer was very similar to this material with the only obvious difference being the presence of water. It is assumed that these two layers are a long chain ketone solution and the long chain ketone itself.

The ball-on-cylinder tests run using cetane and treated cetane are similar to those described previously for diesel fuel. (Due to the small amount of material, no lubricity tests were made on this eluted "polar" component.) The major differences are (1) the lubricity tests were made immediately upon passage through the silica-gel and (2) the effect of bubbling pure nitrogen gas through the system under test was investigated. In one case the treated cetane was pre-equilibrated with N_2 in a conventional gas bubbler while in the other test N_2 was simply passed through the solution while the ball-on-cylinder test was in progress. As shown in Table 13, there seems to be little advantage to this pre-equilibration.

Table 13

Ball-on-Cylinder Data
(32 min., 77°F., 240 RPM)

	Coefficient of Friction			Wear Scar Diameter, mm		
Load, g:	60	120	240	60	120	240
Cetane	0.09	0.16	0.16	0.20	0.26	0.40
Silica-Gel(1) Treated Cetane	0.13	0.25	0.19	0.22	0.61	0.83
Cetane	0.15	0.16	0.16	0.21	0.26	0.40
Silica-Gel(2) Treated Cetane-N_2	0.14	0.15	0.16	0.21	0.41	0.68
Silica-Gel(3) Treated Cetane-N_2	0.13	0.15	0.16	0.22	0.40	0.70
Silica-Gel(4) Treated Cetane	0.14	0.15	0.17	0.31	0.37	0.74

(1) Ball-on-cylinder test run immediately after column treatment.

(2) Test made after one hour equilibration of cetane with N_2 followed by N_2 bubbling during run.

(3) Test made while bubbling N_2 into solution without pre-equilibration.

(4) Test made on treated cetane 24-48 hours after column treatment.

Two cetane runs are reported since two different cylinders were used in this series. With the exception of an unusually low coefficient of friction at 60g for the first cylinder, the results indicate good reproducibility of the lubricity data.

One obvious conclusions is that wear is greater in the silica-gel treated solutions at loads in excess of 60g. Surprisingly, there is little change in the coefficient of friction throughout this series with the only significant difference seen in the silica-gel treated material which was run immediately after column treatment.

The solution yielding the greatest amount of wear is the one tested immediately after column treatment. This result could mean that the presence of trace amounts of water and/or dissolved oxygen may be a critical factor since these species might be expected to equilibrate with the solution through contact with the atmosphere. Other possible lubricity agents, such as aromatics and compounds containing hetero atoms, would not contribute in this manner. It is pertinent to emphasize that the increase in wear with the silica-gel treated materials over the untreated cetane is much greater than the differences between the silica-gel treated samples, indicating the potentially large role which aromatics and hetero-atom containing materials might play. Along with analytical analyses on the column-

treated materials, a series of experiments are planned to evaluate the effect of dissolved oxygen on the lubricating ability of the cetane. Since the levels of interest, both in the case of oxygen and water, are less than 100 ppm, new methods of determination may be devised.

IV. LUBRICITY OF JP-4'S AND EFFECT OF CORROSION INHIBITORS

During this reporting period, information was received from one of the jet engine manufacturers that malfunctioning of a fuel-control valve was occurring in the field. This trouble seemed to have started at about the time that certain changes had been made in the jet fuel at the critical location, one of the changes being that the corrosion inhibitor had been omitted.

To determine whether additives in this low a concentration could have such a pronounced effect, some initial tests were run on the ball-on-cylinder machine. The results indicated that corrosion inhibitors in concentrations as low as 50 ppm (0.005%, 12#/1000 bbl.) could indeed reduce friction, wear, and metallic contact quite noticeably. Because of the importance of the field problem, the effect of corrosion inhibitors is being investigated in some detail. This investigation is also important to the present overall program because the level of additive was much smaller than had previously been considered to have a practical effect on lubricity. In our own earlier work on WS-5412, for example, 2,000 ppm had been found to be required for outstanding gear test performance and 600 ppm for moderately good performance.

Two new elements were introduced by the fuel-control valve problem: (1) load-carrying ability was not the issue, but rather the reduction of friction (reduced adhesion) between closely lapped metal surfaces carrying essentially no load, (2) highly-refined JP-4 fuels could be made commercially which had essentially no lubricity whatsoever. A combination of a "squeaky clean" fuel, no surface-active additive, and a mechanical system capable of high adhesion could cause serious sticking problems. The data reported here is organized as to technical format and not as obtained chronologically.

A. Non-Additive Fuels

Three JP-4 fuel samples from three USAF bases were supplied us by WPAFB. One of these bases (coded A) was from the site of the fuel-control valve trouble. This fuel was found to give substantially higher wear than the other two in the ball-on-cylinder machine, using a steel-on-steel system. Friction was also higher and much more erratic.

Table 14

Ball-On-Cylinder Tests

Steel-On-Steel, 240 rpm, 32 min.

JP-4 Fuel	Wear Scar Diameter, mm			Coef. of Friction		
	60 g	240 g	1 kg	60 g	240 g	1 kg
A	.31	.49	.58	.14*	.16*	.38*
B	.23	.33	.38	.18	.15	.18
C	.22	.27	.34	.13	.15	.18

*Friction more erratic with Fuel A.

Table 15

Ball-on-Cylinder Tests
(Steel-on-Steel, 240 rpm, 77F)

	Wear Scar Diameter, mm							
	Series 1 (32 min.)			Series 2 (64 min.)		Series 3 (64 min)		
JP-4 Fuel	60 g	240 g	1000 g	60 g	240 g	60 g	240 g	Vis/77F, cs
A-1*						0.37	0.55	0.92
A-2*	0.24	0.33	0.46	0.25	0.36			
D		0.31	0.40					0.93
E		0.30	0.44					
F				(0.50)	**			0.99
G				(0.75)	**	0.42		0.96
H				0.26	**			0.94
I						0.33	**	0.77
J						0.29	0.39	0.92
K						0.27	0.32	1.03
L						0.32	0.40	0.94
Reference								
B								0.76
C								0.97
								0.92

* From same base at different times.

** Test discontinued because of excessive friction.

As a result of the ability of the ball-on-cylinder rig to distinguish between fuels, several other JP-4 were sent us for evaluation. Two were furnished us from one engine manufacturer that had reported some high friction and sticking with these fuels in laborstory engine tests. Three were from another engine manufacturer who had had serious flight performance reported on two of the three. Finally, four additional JP-4's from four more USAF bases were sent by WPAFB. The composition of these fuels was not known, nor were there any data on what additives, if any, the fuels contained. Although these data could probably have been obtained analytically, it did not appear that this information would be any particular advantage over the information already being obtained on the ten commercial fuels. The data are being reported here only to illustrate that major differences are found among JP-4's used in the field. In evaluating these fuels on the ball-on-cylinder test, it was found that the wear scar on the ball was an accurate reflection of the frictional behavior. This therefore became the standard method of reporting the data. However, in all cases, the friction traces were closely compared to ensure that the wear scar was in fact indicating the amount of friction. For additive fuels this correlation between wear and friction did not hold, as will be shown later.

Table 15 gives the relative performance of these JP-4's. Fuel F was clearly the worst of the fuels, with Fuel G nearly as bad. These two fuels had the most serious problems reported from the field. Their frictional traces were extremely erratic, often going off-scale. At the higher loads the behavior was so bad that the tests had to be terminated to avoid damaging the spring in the friction-measuring apparatus.

The differences in performance cannot be acribed to viscosity, for most of the fuels were between 0.9 and 1.0 cs. Of the two lowest viscosity fuels, one was quite poor in lubricity, the other was our Reference JP-4 which is exceptionally good. Viscosity at 77F are given in the last column of Table 15, and it can be seen by inspection that there is no correlation.

It is evident that current refining practices can give a fuel that is extremely pure as far as lubricity agents are concerned.

B. Oxidation Inhibitors

A distillation of Fuels A, B and C revealed that the bottoms from Fuels B and C developed a pink color in methanol. This was shown photospectrometrically to be caused by the oxidation inhibitor--N,N'-dialkylparaphenylenediamine--used in these two fuels. To determine whether this additive could have caused the difference between Fuel A and Fuels B and C, a brief study was carried out.

Using Fuel A as a base, the effect of 30 ppm of N,N'-disecondary-butyl-paraphenylenediamine was determined in the ball-on-cylinder rig. The results, given in Table 15, show no decrease in wear scar, nor was there a difference in metallic contact. Friction was quite erratic in all runs, but somewhat smoother and at a slightly lower level with the additive.

Similar tests were carried out in cetane, using 7.5 and 30 ppm of the additive. Again there was no change in wear or metallic contact and in this case the friction traces were actually more erratic than with cetane alone.

(See Table 16 on next page)

Table 16

Antioxidant Has No Effect On Lubricity
Ball-on-Cylinder Tests

Steel-On-Steel, 240 rpm, 32 Min.

Fuel	WSD, mm		
	60 g	240 g	1 kg
JP-4 A	0.24	0.33	0.46
A + 30 ppm N,N'-disecondary-butyl-paraphenylenediamine	0.26*	0.35*	0.48*
Cetane	0.21		
Cetane + 30 ppm same	0.21**		
Cetane + 7.5 ppm same	0.19**		
Cetane + 7.5 ppm N,N'-disalicylidene 1,2 propanediamine	0.21**		

*Friction somewhat less.

**Friction somewhat greater.

It is apparent from the data that the lower friction of fuels B and C is not due to the presence of this antioxidant.

A metal deactivator (N,N'-disalicylidene 1,2 propanediamine) was also tested at 7.5 ppm and also was found to have no effect on lubricity. This is also shown in Table 16.

C. Corrosion Inhibitors

The chief suspect in the sudden rash of field problems seemed logically to be the absence of the corrosion inhibitors. These materials are strong surface-active agents, and therefore would logically be good antifriction agents. In fact, it is precisely their surfactant properties that led to their removal in the first place, for they seriously interfere with water-haze removal. Also, it is well-known that antiwear agents frequently impart rust inhibition to oils.

In the present investigation two rust inhibitors, coded ER-4 and ER-5, have been studied in detail. These two additives are entirely different in chemical composition and, as will be seen, perform quite differently as antifriction additives. Early ball-on-cylinder tests had indicated these two additives both greatly reduced friction of a highly purified fuel. This was confirmed by tests carried out by a jet engine manufacturer, where sticking of the fuel control resulted when a non-additive fuel was used, but could be unstuck if the fuel were changed to one containing one of these corrosion inhibitors. The agreement between these two test methods greatly increased the confidence in each method alone.

Ball-on-cylinder test data are summarized in Tables 17 and 18. It will be seen that both ER-4 and ER-5 reduce friction, with ER-5 being perhaps somewhat

Table 17

Corrosion Inhibitors Are Antifriction Agents

Ball-on-Cylinder Tests
(Steel-on-Steel, 240 rpm, 77F)

Additive		Wear Scar Diameter, mm.							
		Cetane		Ref. JP-4	Fuel D	Fuel A-2		Fuel F	
Load, g:		60	240	60	60	240	1000	60	240
Time, min.		32	32	32	64	16	16	64	64
None		0.21	0.26	0.24	0.29	0.36	0.45	0.50*	**
50 ppm	ER-4	0.21	0.30	0.28	0.27	0.39	0.48		
	ER-5	0.17			0.22			0.26	0.30
	ER-3								0.34
	Oleic Acid					0.23			
25 ppm	ER-5							0.27	**
100 ppm	ER-3					0.28	0.30		
500 ppm	ER-4	0.25							
1 %	ER-4	0.23	0.46						
1%	ER-6					0.36	0.45		

* Excessive chattering.

** Test terminated because of excessive friction.

Table 18

Corrosion Inhibitors Are Antifriction Agents

Ball-on-Cylinder Tests
(Steel-on-Steel, 240 rpm, 77F)

	Coefficient of Friction							
	Cetane		Ref. JP-4	Fuel D	Fuel A-2		Fuel F	
Load, g:	60	240	60	60	240	1000	60	240
Time, min.	32	32	32	64	16	16	64	64
Additive								
None	0.17	0.16	0.23	(1)	(1)	(1)	(1)	**
50 ppm ER-4	0.14	0.14	0.16	(2)	(1)	(2)		
ER-5	0.12			(3)			(2)	(2)
ER-3								(3)
Oleic Acid					(3)			
25 ppm ER-5							(2)	**
100 ppm ER-3					(3)	(3)		
500 ppm ER-4	0.14							
1% ER-4	0.14	0.13						
1% ER-6					(1)	(1)		

(1) Erratic friction trace

(2) Moderately smooth friction trace

(3) Smooth friction trace

** Test terminated because of excessive friction

better. ER-5 also reduces the wear scar as would be expected, inasmuch as it decreases the adhesive friction. This behavior is consistent in two JP-4's and cetane.

ER-4 obviously works differently. Although it is about as good as ER-5 in reducing friction, it actually causes an increase in wear, the increase becoming greater at higher concentrations. At the same time, the metallic contact (measured by electrical resistance) decreases to zero, indicating the formation of an insulating layer between the rubbing surfaces. The higher the concentration of ER-4, the more rapidly the metallic contact decreases to zero. These data are summarized below.

Table 19

Ball-on-Cylinder Tests
(Steel-on-Steel, 60 g, 240 rpm)

ER-4 in Cetane	WSD, mm	Time for Metallic Contact to Decrease to 10%, min	Coeff. of Friction
None	0.21	---	0.17
50 ppm	0.21	18.8	0.14
500 ppm	0.25	8.5	0.14
1%	0.28	1.7	0.14

The action of ER-4 is similar to that of most EP additives. These are known to react rapidly with fresh metal to form an inorganic or partly inorganic layer, usually a sulfide, chloride, phosphate or similar compounds. This compound reduces adhesion and friction, but is soft and easily worn away. By reducing adhesion, these additives prevent scuffing but only at the expense of sacrificial wear. It is evident from the data on ER-4 that the wear scar diameter of such additives is no indication of their anti-friction activity.

The data in Tables 17-18 show that good anti-friction behavior is obtained in most cases with as little as 50 ppm. However, with Fuel F, which is exceptionally poor in lubricity, 50 ppm was not enough to bring this fuel to the level of other JP-4's and 25 ppm of ER-5 gave a failure at 240 load.

It is interesting that the corrosion-inhibitor ER-5 was about as good a lubricity additive as the antiwear additive ER-3. However, oleic acid was even better. On the other hand, adding 1% of a very high viscosity petroleum stock, ER-6, was completely ineffective. This material does not contain any surface-active compounds, and the test is analogous to adding heavy aviation oil to the fuel. It is obvious that in this test the surface-active properties are important.

These tests differ from the actual fuel control unit in three ways: (1) the metals are steel-on-steel whereas in the fuel control both surfaces are hard-anodized aluminum, (2) the speed is constant, whereas the piston in the fuel control is subjected only to periodic motion, and (3) the area of contact is very small and the Hertz load relatively high.

In order to eliminate the first difference, 4150C aluminum cylinders and 4122C aluminum buttons were fabricated and hard anodized. These coatings are much harder than hard steels. Hard anodized aluminum has a surface layer of corundum,

rating 9 on Moh's scale of hardness, which is very roughly about 85 Rockwell C.

The first attempts to get an anodized surface was with aluminum balls and cylinders that were on hand. The alloys were high in copper, and difficult to anodize. The oxide surfaces were poorly adhered. Even so, tests on these parts showed qualitative agreement with the steel-on-steel tests. In comparing the three JP-4's, Fuel A gave a bigger wear scar on the ball, showed some flaking on the cylinder track, and had high and erratic friction throughout the test. Fuels B and C gave smaller scars, and much smoother friction traces for the first 20-25 minutes when they, too, became erratic. Fuel A with 50 ppm of either ER-4 or ER-5 was considerably better in both wear and friction. These data are summarized in Table 20.

Table 20

Ball-on-Cylinder Tests
(Anodized Al (AA-2017) on Anodized Al (AA-2024) 30 g, 60 rpm, 32 min)

Fuel	WSD, mm	Friction
A-1	0.78*	high-erratic
B	0.71	low-smooth for 25 min.
C	0.69	low-smooth for 20 min.
A-1 + 50 ppm ER-4	0.53	low-smooth for entire test
A-1 + 50 ppm ER-5	not defined	low-smooth for entire test

*track shows flaking of anodized surface.

These tests were repeated on another cylinder with the same relative results, although at a different absolute level, due apparently to irreproducibility of the anodized surface. The frictional traces were also different; in this series the coefficient of friction rose rapidly during the first few minutes, then fell off to a steady value of 0.20. The most apparent differences between fuels were the maximum level reached in the early part of the test.

Table 21

Ball-on-Cylinder Tests
(Anodized Al (AA2017) on Anodized Al (AA2024) 30 g, 60 rpm, 32 min)

Additive in Fuel A-2	Max. Coeff. of Friction	WSD, mm
None	1.5	0.57
1% ER-6	1.4	0.43
50 ppm ER-4	1.5, 1.4	0.53, *
50 ppm ER-5	1.0	*
50 ppm Oleic Acid	0.63	*
100 ppm ER-3	0.33**	*

* Scar undefined.

** Friction also less erratic.

It is worth noting that ER-4 did not give a larger wear scar, as it did with steel. Its reaction with Al_2O_3 is obviously different. ER-6, the heavy petroleum stock, again was relatively ineffective even at 1% when compared to ER-5 or oleic acid at 50 ppm. ER-3 at 100 ppm (so chosen to have the same Neut. No. as 50 ppm oleic acid) was considerably better. Obviously more work is needed here at different concentrations, surface interactions, loads and speeds.

The additive tests were repeated using low-copper aluminum alloys (4150C & 4122C) also hard anodized. The surfaces from these alloys were much smoother, blacker, and more adherent. The additive performance, however, was nearly identical to the previous tests.

Table 22

Ball-On-Cylinder Tests

Hard-Anodized Al (Bendix alloys, 4150C & 4122C) 32 min

		WSD, mm			Coeff. of Friction	
	Load g	30	120	240	120	240
	Speed rpm	60	60	240	60	240
Additive in JP-4 A-2						
None		0.33	0.43	0.62	.126	0.142
50 ppm ER-4		0.28	0.40	0.66	.122	0.141
50 ppm ER-5		0.22	0.31	0.52	.106*	0.154*
100 ppm ER-3		0.20	0.32	0.54	.099*	0 140*

*Much smoother friction trace.

ER-4 was not a pro-wear additive, but it was not as effective in reduing friction as either ER-5 or ER-3. Again it indicates that ER-4 works with steel by reaction with the surface. With Al_2O_3 this reaction is impossible and its effectiveness is much less. This points up the fact that good performance in friction and wear is not solely a property of the fuel (lubricity), but rather is a joint property of the fuel and the surface, interacting together.

To test possible stick-slip behavior at slow speeds, still using anodized aluminum, ball-on-cylinder rig was modified by using a reduction gear in the drive mechanism, and driving through a loosely-coupled magnetic coupling. The combination of slow speed and non-rigid coupling gave very pronounced stick-slip. Motion consisted of a series of jerks 1.2 mm long, one every 8 seconds or so. Static friction was about double the dynamic friction.

This test technique showed only minor differences among fuels and additives, although what differences were found agree qualitatively with the higher speed runs. Fuel A was worse than B or C. Fuels A and B responded to ER-4 and ER-5, with ER-5 being better.

It appears that the small area of contact may be defeating the correlation of this test with fuel-control-valve performance. Lapped in surfaces of about 1 sq. cm will be experimented with.

V. FUTURE WORK

Because of the importance of small traces of additives or impurities in friction and wear performance, the pure hydrocarbons obtained in this program will be more carefully purified before running performance tests. In some cases, chromatographic grade hydrocarbons will be used. Otherwise, a heart-cut from a fractional distillation will be followed by silica-gel extraction to remove all polar impurities and leave only the hydrocarbon structure to account for differences. These purified hydrocarbons will also be used to investigate the effect of temperature per se, as separate from the effect of temperature on viscosity.

The analyses of the fuels will be completed with the determination of the aromatic content by chemical type. The effect of adding aromatics to paraffinic fuels will also be studied.

More corrosion inhibitor additives will be examined. Also, concentration studies will be carried out on some of the more effective ones.

The work so far has concentrated on the frictional aspects of lubricity. This predicts sticking or adhesion between lapped surfaces but probably does not predict gear pump performance where anti-scuffing is more important. Therefore scuff loads will be measured in both ball-on-cylinder and four-ball tests.

APPENDIX TABLE I

GAS CHROMATOGRAPHIC ANALYSES OF FUELS[1]

Carbon Number	JP-4	Naphtha	Diesel Fuel
n-C_4		1.45	
C_4		0.02	
n-C_5	1.8	19.56	
C_5	1.4	14.93	
n-C_6	3.8	19.16	
C_6	4.6	30.73	
n-C_7	6.5	2.73	
C_7	11.6	11.19	
n-C_8	5.5	0.04	Trace
C_8	21.3	0.19	0.2
n-C_9	2.7		0.2
C_9	5.7		0.3
n-C_{10}	2.7		0.5
C_{10}	13.1		1.0
n-C_{11}	2.1		1.0
C_{11}	8.3		2.0
n-C_{12}	1.3		2.0
C_{12}	3.9		3.7
n-C_{13}	0.5		4.1
C_{13}	2.3		8.6
n-C_{14}	0.1		5.0
C_{14}	0.4		12.9
n-C_{15}			5.1
C_{15}	0.4		17.0
n-C_{16}			4.6
C_{16}			15.7
n-C_{17}			2.7
C_{17}			13.1
n-C_{18}			--
C_{18}			0.2

APPENDIX TABLE I (Cont.)

GAS CHROMATOGRAPHIC ANALYSIS OF FUELS[1]

Carbon Number	P&W 523	JP-5	75 LN-LV	RAF-176-64	AFFB-3-65	RAF-173-61	Bayol[3] 35
n-C_9[2]		0.2		1.1	1.5	0.1	
C_9		0.6		4.0	6.8	0.5	
n-C_{10}		1.2	2.9	3.7	1.5	0.3	
C_{10}		1.7	2.7	10.4	42.6	17.6	0.2
n-C_{11}	5.5	6.2	12.5	3.8	1.4	0.4	
C_{11}	6.5	8.6	43.4	16.1	35.7	18.0	13.4
n-C_{12}	9.0	12.3	3.0	3.2	0.2	0.2	
C_{12}	25.0	24.3	35.1	13.1	8.9	22.1	41.3
n-C_{13}	6.5	4.2	0.5	3.1	0.1	0.2	
C_{13}	28.0	28.3	8.6	14.1	1.0	23.8	34.5
n-C_{14}	2.7	0.9		2.5	0.1	0.1	
C_{14}	14.6	9.2	0.3	11.2	0.1	12.7	10.6
n-C_{15}		0.1		0.8			
C_{15}	2.2	2.1		9.2	0.1	4.0	
n-C_{16}							
C_{16}		0.1		3.7			

(1) GC Analysis via Perkin-Elmer 226; 300' Column, DC 550.

(2) Normal hydrocarbons as reported are a maximum value and may include other unresolvable compounds.

(3) Normal paraffinic content of Bayol 35 too low for estimation.

APPENDIX
TABLE II

CHEMICAL COMPOSITION OF PUMP PARTS

	Vane %	Ring %
C	0.8	1.0
Mn	0.3	0.4
Cu	0.1	0.2
Si	0.2	0.3
Fe	83.8	96.5
Ni	0.2	-
Cr	4.5	1.4
Mo	4.3	-
W	5.6	-
V	0.1	-